

XIII. *On the Osmotic Pressures of Calcium Ferrocyanide Solutions.*
Part II.—Weak Solutions.

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IN the following communication the experiments on the direct measurements of the osmotic pressure and the densities have been carried out in conjunction with Mr. HARTLEY, while those on the electric conductivities were with Mr. STEPHENSON.

The reason for choosing calcium ferrocyanide as solute were given in Part I., but it may be added that weak solutions of this salt showed certain interesting anomalies, to be described later, which made it desirable to measure their electric conductivities with a view to throwing some light on the connection between osmotic pressure and ionisation.

The process followed in purifying the salt has already been given in Part I.,* and so has that used in obtaining the densities.

The Measurements of Osmotic Equilibrium Pressures.

These measurements are confined to solutions whose equilibrium pressures are under 25 atmospheres. The apparatus was the same as that previously described in the account of our experiments on sugar solutions ('Phil. Trans.,' Series A, vol. 206, p. 482), except that the large dead-weight pressure-gauge was replaced by a smaller one specially made by Messrs. Schäffer and Budenberg, which seemingly allowed accurate measurements to be obtained down to 2·5 atmospheres pressure, and at the same time the increment of pressure (*loc. cit.*, p. 498) was 0·1 atmosphere.†

It had been thought that by increasing the area of the membrane (but keeping the general construction of the apparatus the same) these lower pressures would be measurable to a greater degree of accuracy—that is to say, that for a small change in pressure a larger quantity of water would pass through the membrane and consequently give a bigger effect on the reading of the water-gauge. Some 50 porcelain tubes, supposed to be similar to those used previously in paste porosity and diameter (but 20 cm. in length), were therefore obtained from the makers. Unfortunately all efforts to obtain even one membrane good enough for accurate work failed, and the attempt has had to be abandoned for the time being; consequently the experiments were done with the short tubes.

* 'Phil. Trans.,' Series A, vol. 209, p. 179.

† This apparatus was compared with the mercury column at the National Physical Laboratory and found correct.

TABLE I.—Calcium Ferrocyanide.

(1.) Date.	(2.) Weight concentra- tion.	(3.) Density at 0° C.	(4.) Percentage of Aq.	(5.) Tube.	(6.) Apparent turning- point.	(7.) Guard-ring leak.	(8.) Duration of experiment.	(9.) Solution leak.	(10.) Rate of movement of water-level in millimetres of gauge per 15 minutes per increment of 0.1 pressure in atmo- sphere.	(11.) Turning- point corrected for guard- ring leak = equilibrium pressure in atmo- spheres.
*November 6, 1907 .	21.808	1.16279	39.92	N	20.37	0.0	3 $\frac{1}{4}$	Nil	3.4†	20.37
*November 18, 1907 .	21.819	1.16295	39.91	X	20.31	0.15	2	Nil	6.2†	20.30
February 10, 1908 .	17.616	1.13449	39.98	X	14.69	0.8	3 $\frac{1}{4}$	Nil	1.5	14.63
March 12, 1908 . . .	17.603	1.13439	39.98	N	14.72	0.8	—	Not determined	1.5	14.66
*March 12, 1908 . . .	17.603	1.13439	39.98	N	14.70	0.8	—	—	4.0†	14.63
January 31, 1908 . . .	12.210	1.09588	39.99	X	9.21	0.2	4 $\frac{3}{4}$	0.0010	1.45	9.20
February 14, 1908 .	12.216	1.09597	39.98	N	9.24	0.45	3 $\frac{3}{4}$	Nil	1.05	9.20
December 4, 1907 . .	7.074	1.05715	39.95	N	5.30	0.0	3	—	0.8	5.30
December 10, 1907 .	7.070	1.05717	39.98	N	5.41	0.5	3	0.0010	1.15	5.37

† The increment of pressure is 0.34 atmosphere.

The experiments marked * were made with the larger dead-weight apparatus, while the remainder were made with the new apparatus mentioned on p. 319. The second experiment of March 12, 1908, was obtained with the larger apparatus after the determination with the smaller, the same solution being used; in fact, the osmotic apparatus containing solution and tube, &c., was merely transferred from one to the other, and the fact that the two experiments agree so closely, although the pressure increments are different, seems to show that the method of obtaining the null-point ('Phil. Trans.,' A, vol. 206, p. 491) is sufficiently accurate.

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Results of Density and Equilibrium Pressure Measurements.

The foregoing table gives the results obtained :—Column (1) gives the date ; (2) the weight concentration, *i.e.* the number of grammes of anhydrous salt to 100 gr. of water ; (3) the density of the solution at 0° C. ; (4) the percentage content of water in the hydrated salt ; (5) the tube employed ; (6) the apparent turning-point, that is, the point at which there was no observable movement of the water-level in the gauge ; (7) the guard-ring leak (see Part I.) ; (8) the time the pressure was on the solution ; (9) the quantity of anhydrous salt passed through the membrane ; (10) the change in the water-level caused by the increment of pressure ; (11) the apparent turning-point corrected for guard-ring leak ; in this case it is the equilibrium pressure.

The following table gives the mean values derived from Table I., together with the theoretical osmotic pressures calculated on the assumption that BOYLE'S law holds for these solutions.

Column (1) gives the weight concentration, *i.e.* the number of grammes of solute to 100 gr. of solvent ; (2) gives the corresponding densities ; (3) the number of gram-molecules of anhydrous salt in the litre of solution ; (4) the corresponding equilibrium pressures ; (5) the osmotic pressure calculated from BOYLE'S law, assuming $RT = 22.41$.

All molecular weights have been calculated with $H = 1$.

TABLE II.

(1.)	(2.)	(3.)	(4.)	(5.)
Weight concentration.	Density at 0° C.	Number of gram-molecules of anhydrous salt in litre of solution.	Observed equilibrium pressure.	Osmotic pressure (BOYLE'S law).
21.813	1.16287	0.7175	atmospheres 20.33	atmospheres 16.08
17.610	1.13444	0.5853	14.65	13.11
12.213	1.09592	0.4110	9.20	9.21
7.072	1.05716	0.2406	5.34	5.39

The agreement at the two lower concentrations between the BOYLE'S law osmotic pressures and those directly observed is remarkable. But as calcium ferrocyanide solutions are conductors of electricity, and therefore presumably ionised to a considerable extent, we should expect the observed osmotic equilibrium pressures to be higher than the calculated. This discrepancy led to similar work being done on solutions of strontium and potassium ferrocyanides, and the following tables give the results.

TABLE III.—Potassium Ferrocyanide.

(1.) Date.	(2.) Weight concentration. Number of grammes of anhydrous salt to 100 gr. Aq.	(3.) Density at 0° C.	(5.) Tube.	(6.) Turning- point.	(7.) Guard- ring leak.	(8.) Duration of experiment in hours.	(9.) Solution leak.	(10.) Rate of movement of water in millimetres per 15 minutes per 0.1 atmosphere.	(11.) Turning-point corrected for guard-ring leak = equilibrium pressure.
March 13, 1908 . . .	13.583	1.08575	X	atmospheres 19.32	0.5	4½	Not determined	1.4	19.29
January 3, 1908 . . .	13.576	1.08574	N	19.26	0.6	4	Nil	1.15	19.20
March 16, 1908 . . .	8.899	1.05817	N	13.56	0.6	4½	Not determined	1.35	13.51
December 27, 1907 . . .	8.895	1.05803	N	13.58	0.5	3	Nil	0.9	13.52
March 6, 1908 . . .	5.631	1.03775	N	9.20	0.45	4	Not determined	1.2	9.19
January 8, 1908 . . .	5.630	1.03771	X	9.20	*	4½	Nil		*
March 10, 1908 . . .	3.119	1.02133	X	5.61	0.1	3½	Not determined	0.75	5.53
March 5, 1908 . . .	2.957	1.02038	X	5.30	0.6	4½	Not determined	1.2	5.29
December 21, 1908 . . .	1.518	1.01050	X	2.90	+0.3	4	Nil	1.6	2.93

* This experiment was rejected, as it was found that the guard-ring leak had not been determined properly.

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The meaning and numbering of the columns are the same as in Table I., with the exception that for the potassium salt column (4) is omitted because the salt, which was purchased as Messrs. Kahlbaum's purest, was not systematically analysed* for its water content.

In the following table the mean values are given, and the columns are numbered and have the same significance as in Table II.

TABLE IV.

(1.)	(2.)	(3.)	(4.)	(5.)
Weight concentration.	Density.	Number of gram-molecules per litre.	Observed equilibrium pressure.	Osmotic pressure (BOYLE'S law).
13·580	1·08575	0·3547	atmospheres 19·25	atmospheres 7·95
8·897	1·05810	0·2362	13·52	5·29
5·631	1·03775	0·1512	9·19	3·39
3·035	1·02085	0·08216	5·41	1·84
1·518	1·01050	0·04129	2·93	0·93

It will be noticed that these results are such as would be expected on the dissociation hypothesis; the greater the dilution the greater the ionisation, until at the greatest dilution there is apparently dissociation into about three ions or molecules.

A few experiments were made with strontium ferrocyanide to see whether the same anomalies (see p. 321) obtained as those shown by the calcium salt. The salt was purchased from Messrs. Kahlbaum and purified by recrystallisation as in the case of the calcium salt.

Analyses gave the following results:—

	1st lot from Kahlbaum.	2nd lot from Kahlbaum.	1st lot recrystallised.	2nd lot recrystallised.		Percentage composition calculated from salt containing—	
						15 Aq.	14 Aq.
Sr	per cent. 27·28	per cent. 27·15	per cent. 27·47	per cent.	per cent. 27·97	per cent. 26·64	per cent. 27·39
Fe(CN) ₆	32·87		33·02		33·69	32·28	33·19
H ₂ O	38·86	38·89	39·31	39·40	37·80†	41·08	39·42
	99·02		99·80		99·46	100·00	100·00

* An analysis of the salt gave 12·81 per cent. H₂O. Theoretical 12·78 per cent.

† The sample was taken from a lot which was known to have been overdried.

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It will be apparent that the salt when dried in an air current, at about 20° C., contains 14 of water, and not 15 as stated by ROSCOE and SCHORLEMMER.*

The following table gives the results of the osmotic-pressure determinations, and the figures in the columns have the same meaning as in the case of Table I.

TABLE V.—Strontium Ferrocyanide.

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)	(8.)	(9.)	(10.)	(11.)
Date.	Weight concentration.	Density at 0° C.	Percentage of Aq in salt.	Tube.	Apparent turning point.	Guard-ring leak.	Time.	Solution leak.	Rate of movement.	Equilibrium pressure.
					atmospheres		hours		mm.	atmospheres
Nov. 23, 1908	23·99	1·19253	37·83	N	12·07	-0·3	3	Nil	1·3	12·04
Dec. 4, 1908.	17·97	1·14690	38·60	N	8·58	+0·1	2 $\frac{3}{4}$	Nil	1·0	8·59
July 21, 1908	13·51	1·11314	39·31	N	6·40	-0·2	3	0·0004	0·9	6·38
Nov. 10, 1908	12·51	1·10470	37·87	N	5·98	0	8	Nil	1·7	5·98
Nov. 26, 1908	6·199	1·05302	37·79	X	3·38	+0·2	3	Nil	1·6	3·39
Dec. 29, 1908	6·161	1·05281	38·90	N	3·40	0	3		1·5	3·40

Tabulating these results in the form given for the calcium and potassium salts, we get :—

TABLE VI.—Strontium Ferrocyanide.

(1.)	(2.)	(3.)	(4.)	(5.)
Weight concentration. Number of grammes of salt in 100 Aq.	Density at 0° C.	Gram-molecules in the litre of solution.	Observed equilibrium pressure.	Osmotic pressure (BOYLE'S law).
			atmospheres	atmospheres
23·99	1·19253	0·6000	12·04	13·45
17·97	1·14690	0·4542	8·59	10·18
13·01	1·10892	0·3320	6·18	7·44
6·180	1·05291	0·1594	3·40	3·57

In the case of this salt the observed osmotic equilibrium pressures are *less* than those calculated from BOYLE'S law; thus the peculiarity noticed in the case of the calcium salt is emphasised in the strontium solutions.

A search for a similar anomaly was made among such other salts of complex acids

* 'Treatise on Chemistry,' vol. ii., p. 1025 (1897 edition).

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as would be likely to give satisfactory osmotic pressures, but without results, as will be seen by the following list :—*

Substance.	Observed equilibrium pressure at 0° C.	Osmotic pressure (BOYLE'S law).	Remarks.
	atmospheres	atmospheres	
Magnesium camphorate. . .	7·85	7·61†	Preliminary experiment.
" " . . .	5·91	4·36	Accurate osmotic pressure of recrystallised salt.
" " " " . . .	6·09	4·33	" " " "
Potash alum . . .	2·13	0·682	Accurate osmotic pressure.
Sodium naphthionate . . .	9·4	6·32	Preliminary experiment.
" " " " . . .	10·07	6·34	Accurate osmotic pressure of recrystallised salt.
Barium benzene sulphonate .	13·0	5·75	Preliminary experiment.
" " " " . . .	13·86	5·72	Accurate osmotic pressure of recrystallised salt.
Lead benzene sulphonate . .	12·48	5·16	Preliminary experiment.
Potassium benzene sulphonate	15·81	8·69	"
Barium o-nitrobenzoate. . .	16·85	6·63	"
" " " " . . .	16·01	6·20	Accurate osmotic pressure of recrystallised salt.
Calcium naphthionate . . .	3·75	1·85	Preliminary experiment.
" " " " . . .	3·95	1·79	Accurate osmotic pressure of recrystallised salt.
Luteo cobalt chloride . . .	6·67	2·94	Preliminary experiment.
Calcium acetate . . .	5·20	2·36	Accurate osmotic pressure not recrystallised.
" " " " . . .	29·46	13·26	" " "

† This experiment was done with an imperfect membrane.

The Electric Conductivities of the Solutions.

The cell used for the stronger solutions is shown in fig. 1 ; it was originally designed for another research (the conductivities of saturated solutions), but was found quite satisfactory for the present purpose. A is the cell proper, and B and C its electrodes ; these are covered with platinum black in the usual manner. The solution, which is contained in the beaker D (capacity about 250 c.c.), is sucked up into the cell by means of the tap E, and the resistance is determined by the Fitzpatrick and Whetham commutating method.†

As the osmotic pressures were determined at 0° C., it was imperative, for the purpose of comparison, to obtain the conductivities at the same temperature. This was secured in the following way :—The whole apparatus was plunged into ice and the stirrer started ; when the temperature was constant at or near 0° C., the solution was sucked up into the cell and its resistance determined ; the cell was then emptied ; after an interval of three or four minutes it was refilled and the resistance re-determined. These operations were repeated until a constant resistance was obtained. The temperature was always noted before and after every operation, and observations in which there had been a change of more than 0°·01 C. were rejected ;

* We are now experimenting with the ferricyanides for the same purpose.

† 'Phil. Trans.,' A, vol. 194, p. 330.

such a change very seldom happened when the proper level of the liquid in the beaker had been found. The first observation, however, of any series was nearly always somewhat different from the subsequent ones; this was thought to be caused by a slight difference of concentration on the electrode surfaces when first wetted by the solution, and the observation was therefore rejected.

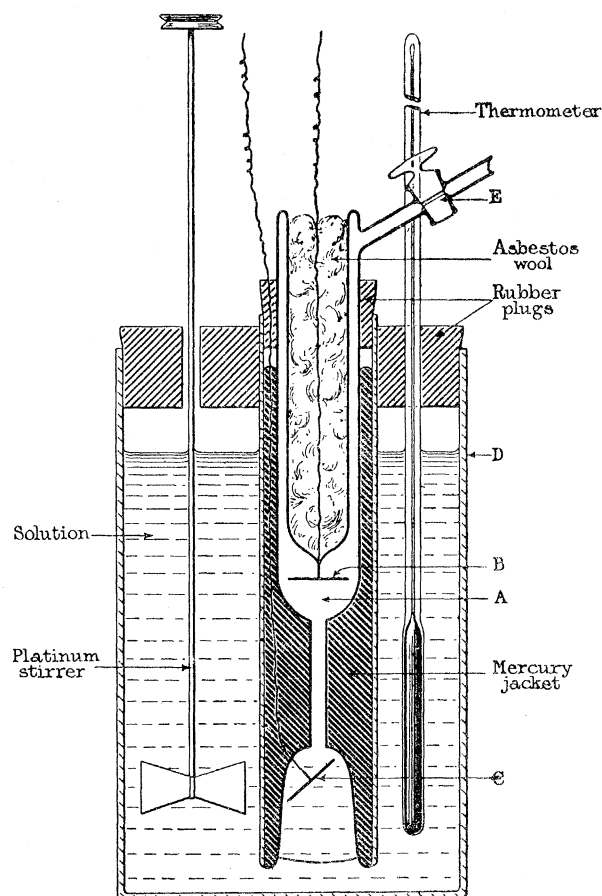


Fig. 1.

Temperature Coefficient.

As the temperature of the solution was always some seven or eight hundredths of a degree above 0° C., a correction was obtained by allowing the temperature to rise slightly and then re-determining the resistance; by assuming that the change of resistance was proportional to the change of temperature the observed resistance could be extrapolated to 0° C.

It may be mentioned here that although the level of the solution in the cell could not be seen on account of the mercury jacket (see fig. 1), yet by means of an oil gauge attached to E it was ensured that on filling the cell the level always reached the same height.

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Resistance Box.

The coils of the box were of manganin, and were tested by means of a calibrated platinum bridge wire having a standard-ohm coil joined to each end. Coils of the same nominal value were thus compared and the results calculated in terms of the coil of highest resistance (5000 ohms), thus giving the value of a box ohm. In no case was the deviation greater than $\frac{1}{2000}$ th of the nominal value.

Resistance Capacity of the Cell.

The cell was standardised by means of an approximately normal solution of potassium chloride. The specific conductivity of this solution is given by Kohlrausch (see LANDOLT and BÖRNSTEIN'S tables) for temperatures from 0° C. upwards. The salt used was Merck's purest, and care was taken that it was thoroughly dry before weighing out the necessary quantity.

Three separate sets of observations were made and the results are tabulated below :—

Concentration. Grammes of KCl in 100 gr. solution.	Resistance in ohms at 0° C.	Specific conductivity of the solutions at 0° C.	Resistance capacity of cell.
		cm ⁻¹ ohm ⁻¹	ohms
7·1322	1360·2	0·06535	88·89
7·1357	1359·2	0·06538	88·87
7·1386	1359·4	0·06541	88·92

A normal solution of potassium chloride contains 7·1385 gr. of salt in 100 gr. of solution and has a specific conductivity of 0·06541 at 0° C. ; the specific conductivities given in the table are calculated from this by assuming that the conductivity is proportional to the concentration.

It is worth noting that on increasing the speed of revolution of the commutator so that the alternations of current were changed from 36 to 72 per second no appreciable change in the resistance of the solution was engendered.

Resistance of the Solutions.

As there was but little salt at our disposal the solutions were made up in the following way: The salt for the strongest solution required was weighed out (a suitable portion from the same bottle being set aside for the analysis of its water content) and the weight of water added determined on the balance. A part of this solution was used for the resistance experiments, and the other part, after weighing, was diluted and again weighed, and so on; thus the weight concentration of each solution used for the conductivity work was known, and the density corresponding to

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the concentration could be obtained from the graph of these two quantities which had already been determined in the osmotic-pressure experiments.

The water used for the dilution was distilled, in a Jena glass still, from a dilute solution of potassium di-chromate, and its resistance determined in another cell to be described later.

The table on p. 329 is a copy of the record of a typical experiment with calcium ferrocyanide.

The columns 1, 2, and 3, under the heading temperature, require a word of explanation. The temperature under 1 is that of the solution just before the cell was filled, 2 gives it just after the measurement of the resistance, and 3 just after emptying.

The solution contained 0.93023 gr. of anhydrous calcium ferrocyanide in 100 gr. of solution.

The ratio arms were 10 : 100 and the battery gave 2 volts.

Resistance of the Solutions at Infinite Dilution.

Although, as is well known, the relation between the conductivity at infinite dilution and that at finite concentrations is not well established for salts of the molecular complexity of the ferrocyanides, yet it was thought that this relation might throw some light on the discrepancy indicated on p. 321. Experiments on very dilute solutions were therefore undertaken.

Low-resistance Cell.

A cell for this purpose was kindly lent by Mr. WHETHAM; it was made of Jena glass and is shown in fig. 2. The electrodes D and E are coated with platinum "grey" to prevent the absorption of salt, which, as pointed out by WHETHAM,* generally takes place when platinum black is used. The cell was suspended in a beaker of ice and water, and this in its turn was placed in ice.

Make up of the Solutions.

The water used was twice distilled in the ordinary way and then redistilled from potassium di-chromate, the middle third only being used. All glass vessels and pipettes were of Jena glass and the water and solutions were stored in stoppered Jena glass flasks.

Resistance Capacity of the Cell.

The cell was standardised by means of a solution of potassium chloride containing 0.007352 gr. of salt in 100 gr. solution. This solution was obtained as follows: A

* *Loc. cit.*

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Time.	Temperature of the solution.			Galvano- meter zero.	Deflection of galvanometer.		Box resist- ance.	Resist- ance of solution.	Remarks.
	1.	2.	3.		Left key down.	Right key down.			
P.M.	° C.	° C.	° C.	—	—	—	ohms	ohms	
1.0	—	—	—	0	0.2R	0.2L	3332	—	Made up solution. } Rejected.
5.20	0.285	0.280	0.285	0	0.1R	0.05L	3333	—	
				0	0.1L	0.1R	3334	33334	
5.26	0.285	0.285	0.285	0	0.1L	0.1R	3334	3333	
				0	0	0	3333	33330	
5.31	0.290	0.285	0.285	0	0	0.05R	3333	33328	
				0	0.1R	0.1L	3332	33328	
5.36	0.290	0.285	0.285	0	0.1R	0.1L	3332	33330	
				0	0	0	3333	33330	
5.41	0.290	0.285	0.290	0	0	0	3333	33330	
				0	0.1R	0.1L	3332	33330	
Mean =	0.289						Mean =	33330	
6.32	0.320	0.310	0.320	0	0	0	3332	—	} Rejected.
				0	0.1L	0.1R	3333	33320	
6.37	0.325	0.315	0.325	0	0	0	3330	33300	
				0	0.1R	0.1L	3329	33300	
6.42	0.325	0.320	0.330	0	0.1R	0.1L	3329	33300	
				0	0	0	3330	33300	
6.47	0.330	0.325	0.330	0	0.2L	0.2R	3331	33293	
				0	0.1L	0.1R	3330	33293	
				0	0.05R	0.05L	3329	33293	
Mean =	0.327						Mean =	33298	

The emergent column correction was -0.038 ,, thermometer zero ,, ,, -0.175 Total -0.213 For the 1st set of observations the true mean temperature was $0^{\circ}.076$ C.; mean resistance, 33330 ohms.,, 2nd ,, ,, ,, ,, ,, $0^{\circ}.114$,, ,, 33298 ,,For a change of temperature of $0^{\circ}.038$ C. the change of resistance was 32 ohms.Therefore taking the mean of all the observations, and correcting for temperature, the resistance of the solution at 0° C. was 33393 ohms.

solution of N/25 was first made up accurately by weight; 10 gr. of this was added to 400 gr. of conductivity water in flask A. At the same time as the water was added to flask A, a similar quantity of the same water was poured into flask B. Both flasks were kept stoppered, and whenever one flask was opened for any purpose the other was opened for the same length of time and in the same place. In this way it was

hoped that any contamination from the atmosphere would affect both equally, and by determining the resistances of the water and solution in the following order—water, solution, water, solution, water—and taking the mean values, we should thus get a close approximation to the conductivity of the salt in the cell.

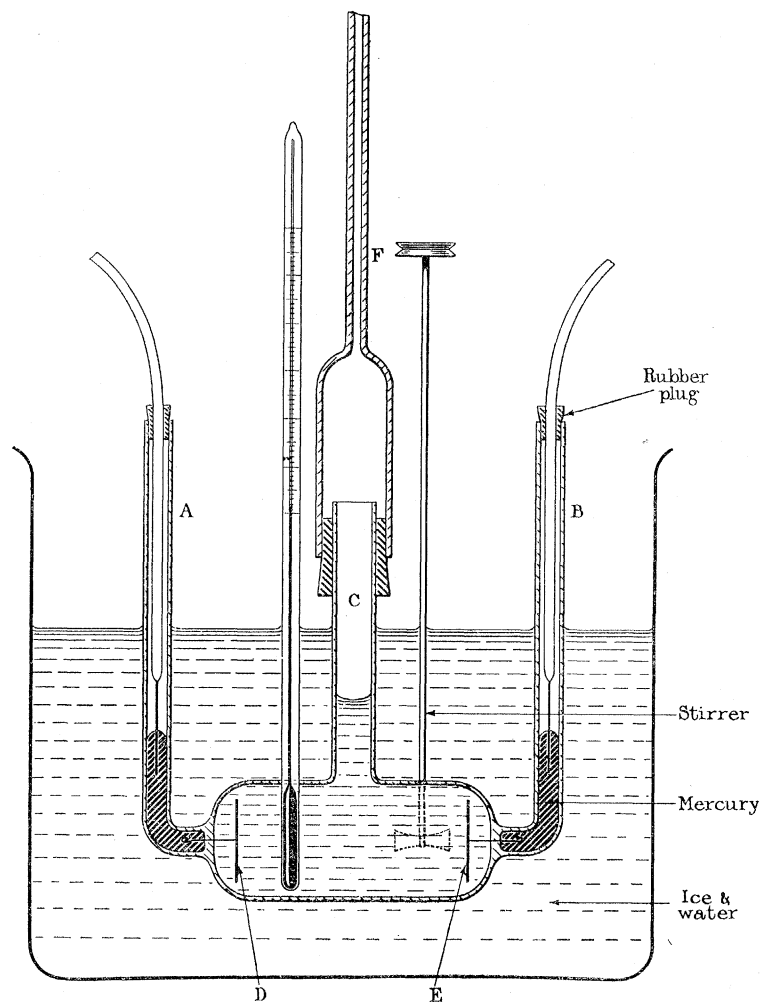


Fig. 2.

Using Kohlrausch's* value for the conductivity of N/1000 potassium chloride (reduced to 0° C. by means of DÉGUISNE's temperature coefficient†) and correcting it for the slight difference in concentration between N/1000 and our solution, we get the resistance capacity of the cell = 0.4539 ohms.

Resistance of the very Dilute Solutions.

A stock solution of each salt was made up and this was used as in the case of the standard potassium solution; it was found, however, that all of the very dilute

* LANDOLT and BÖRNSTEIN's tables, 1905, p. 756.

† LANDOLT and BÖRNSTEIN's tables, 1905, p. 755.

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solutions decreased slightly in resistance with lapse of time, except the most dilute of all, which increased with the time.* In each case a time coefficient was determined by experiment, and the resistances given in the tables are the resistances the solutions would have had immediately after being made up.

It was also noticed that, with the low-resistance cell, the rate of alternation of current had a perceptible effect on the resistance; a great number of experiments were made to determine the cause of this, but without result. It was, therefore, decided to make all measurements at a speed which, on the whole, gave the most consistent results.

Results for Calcium Ferrocyanide.

The results for the calcium ferrocyanide are collected in the following table. The first seven lines refer to solutions whose constants were determined in the high-resistance cell and the remainder refer to the low-resistance cell.

TABLE VII.

Weight of salt in 100 gr. of water.	Number of gramme equivalents in the litre.	Specific conductivity of the solution at 0° C.	Specific conductivity of the water at 0° C.	Specific conductivity of the salt in the solution at 0° C.	Equivalent conductivity of the salt at 0° C.
17.779	2.3632	em. ⁻¹ ohm ⁻¹ 0.03545	—	0.03545	0.01500
7.1265	0.9696	0.01782	—	0.01782	0.01838
3.6294	0.4972	0.029492	—	0.029492	0.01909
1.8570	0.2552	0.024998	0.0520	0.024996	0.01957
0.9390	0.1292	0.022661	0.0514	0.022660	0.02059
0.4385	0.06040	0.021369	0.0515	0.021368	0.02265
0.2109	0.02906	0.037470	0.0510	0.037460	0.02567
0.021794	0.03004	0.031259	0.050965	0.031249	0.04158
0.010875	0.021499	0.047349	0.050959	0.047253	0.04839
0.007245	0.039986	0.045357	0.050937	0.045263	0.05270
0.004345	0.035989	0.043584	0.051005	0.043484	0.05817
0.002413	0.03326	0.042225	0.050981	0.042127	0.06395
0.001204	0.031660	0.041254	0.051068	0.041147	0.06910

The equivalent conductivities of the stronger solutions are plotted against the concentrations in diagram 1, and those of the very dilute solutions are plotted against the cube root of the concentrations in diagram 2; the latter curve when extrapolated, as shown by the dotted lines, to infinite dilution gives the probable limits between

* The greatest decrease observed was 0.03 per cent. per hour, while the increase in the most dilute solution of the calcium salt was 0.10 per cent. per hour, and for the strontium salt 0.14 per cent.

which the value of the equivalent conductivity at that dilution ($= \mu_{\infty}$) lies; that is, between 0.074 and 0.09.

Results for Strontium Ferrocyanide.

These results are given in Table VIII. The first five lines refer to the stronger solutions; they practically cover the range over which the osmotic pressures were measured, and thus, in conjunction with the equivalent conductivity at infinite dilution, afford an insight into the relative dissociation of the salt. The last six lines refer to the very dilute solutions.

TABLE VIII.

Weight of salt in 100 gr. of water.	Number of gramme equivalents in the litre.	Specific conductivity of the solution at 0° C.	Specific conductivity of the water at 0° C.	Specific conductivity of the salt in the solution at 0° C.	Equivalent conductivity of the salt at 0° C.
		cm. ⁻¹ ohm ⁻¹	cm. ⁻¹ ohm ⁻¹	cm. ⁻¹ ohm ⁻¹	
24.016	2.4019	0.03487	—	0.03487	0.01452
13.398	1.3662	0.02316	—	0.02316	0.01695
10.288	1.0548	0.01847	—	0.01847	0.01751
7.3265	0.7545	0.01356	—	0.01356	0.01797
3.7169	0.3849	0.007116	—	0.007116	0.01849
0.03040	0.03162	0.001291	0.001018	0.001281	0.04051
0.01517	0.01577	0.0047730	0.0051055	0.0047624	0.04834
0.01010	0.01051	0.005549	0.0050981	0.005451	0.05187
0.006058	0.006301	0.0043724	0.0051039	0.0043620	0.05745
0.003364	0.003499	0.002336	0.0051057	0.002230	0.06373
0.001678	0.001746	0.001337	0.0051086	0.001228	0.07035

The numbers are plotted in diagrams 1 and 2 in the same way as in the case of the calcium salt.

From the curve of the very dilute solutions the value at infinite dilution will be seen to lie between 0.076 and 0.098.

Theoretical Considerations.

From the foregoing conductivity results it will be seen that both the calcium and the strontium solutions are fair conductors of electricity, yet if we judge from the osmotic-pressure experiments alone, the calcium salt should show no appreciable dissociation, while the strontium salt shows that there must even be some association.

A tentative explanation of these facts may be based on either of two hypotheses :

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(1) that the salts in solution are associated* into double molecules, and these are ionised, or (2) that the salts are ionised single molecules, and the ions are themselves aggregated into larger complexes.

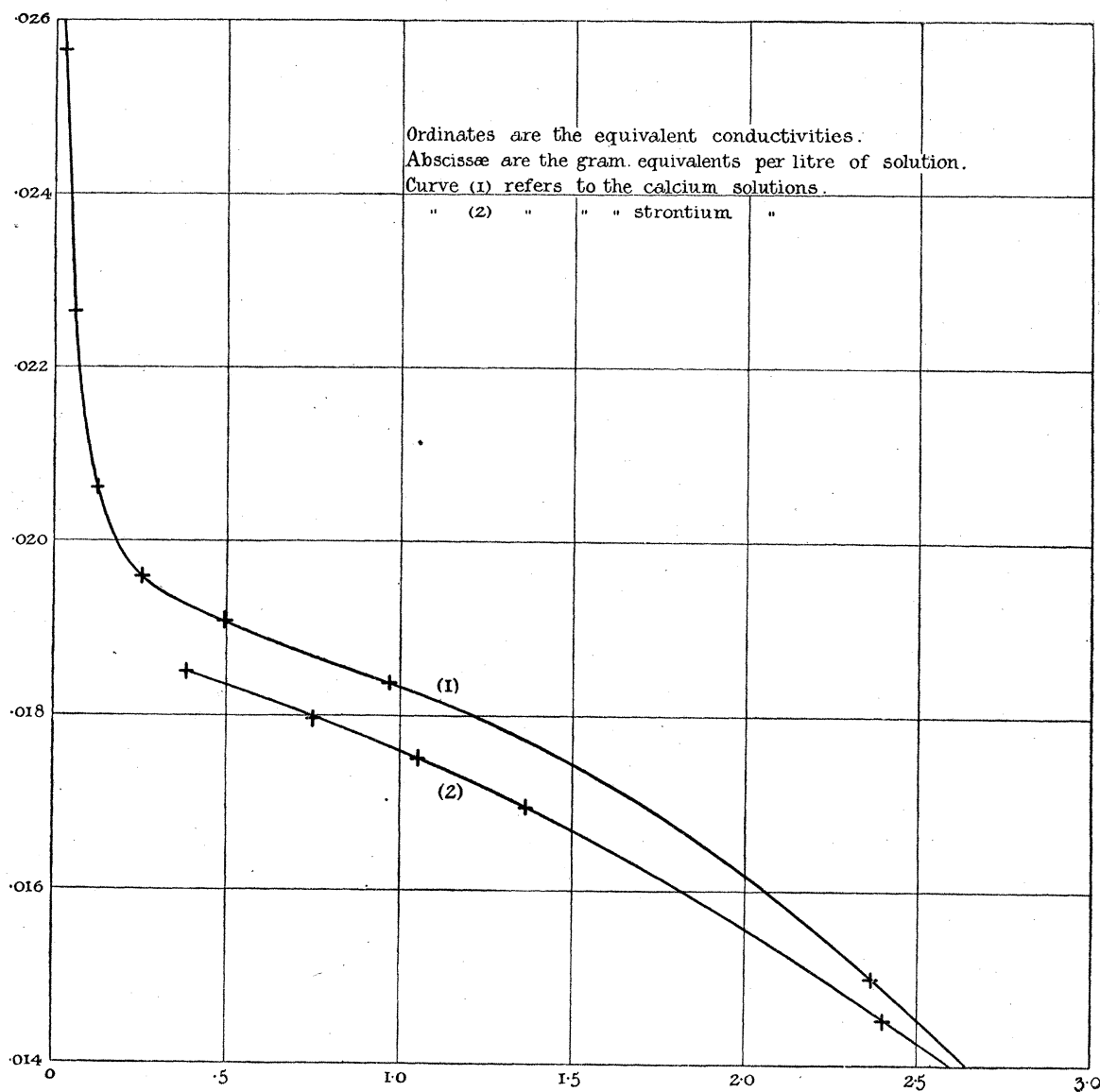


Diagram 1.

The first hypothesis is the more simple (it admits of a suitable chemical formula being postulated), and if by its aid we can explain the facts, it will not be necessary to consider the second.

Assuming, then, that the molecules are double, we shall get the following tables, in

* *Cp.* RAOULT ("Tonometrie," 'Scientia Series,' No. 8, p. 90) on the association of the sulphates of divalent metals as evidenced by the lowering of the vapour pressures of the solutions.

which column (1) gives the weight concentration; (2) the number of double gram-molecules in the litre of solution ($= N$); (3) the equivalent conductivity of the solution ($= \mu$); (4) the ratio μ/μ_∞ , where μ_∞ is the equivalent conductivity at infinite

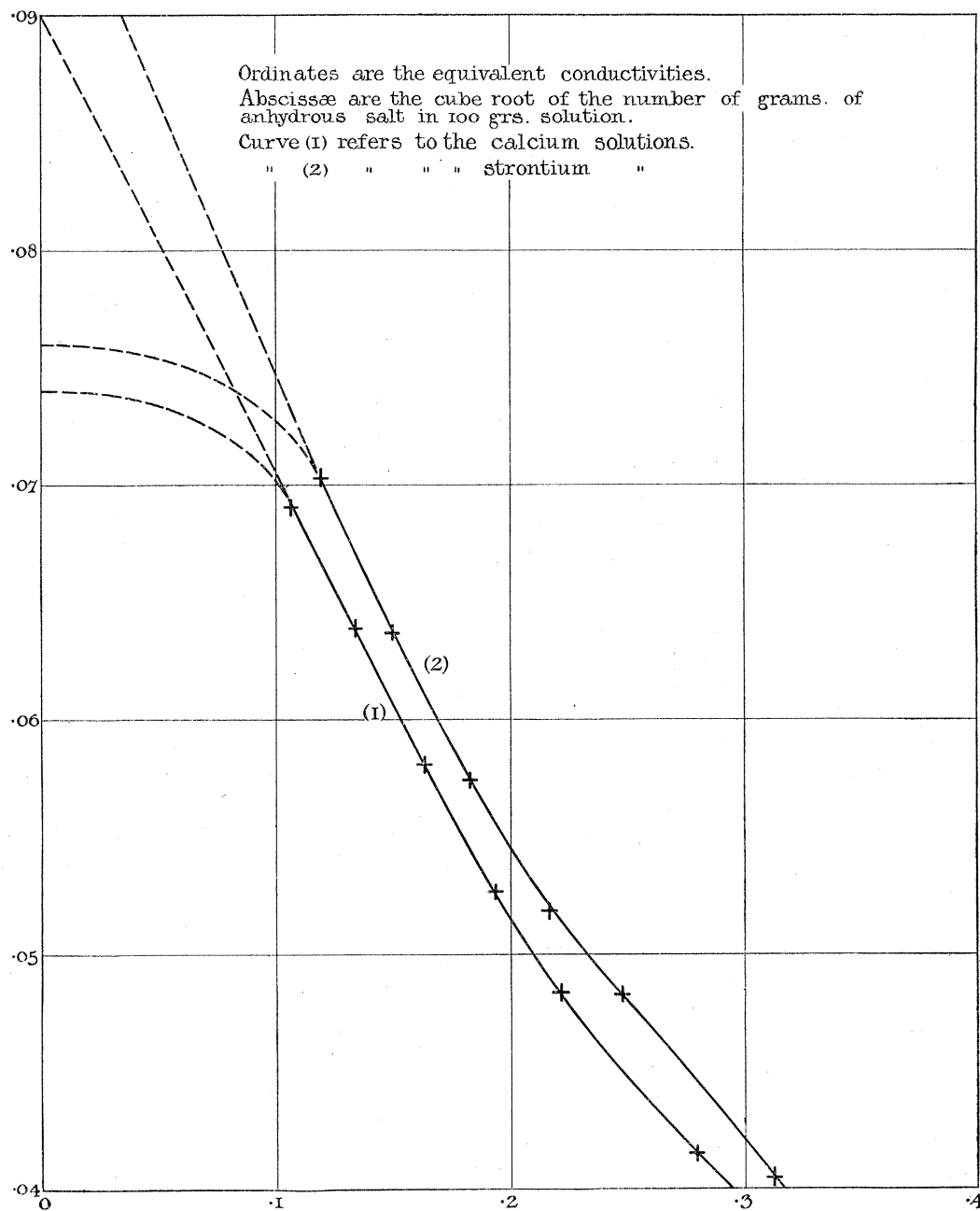


Diagram 2.

dilution, and is assumed to be the mean of the limits given by the curves on diagram (2); (5) gives the osmotic pressure ($= P$) calculated from the well-known equation

$$P = RT \cdot N \{1 + (n-1) \mu/\mu_\infty\},$$

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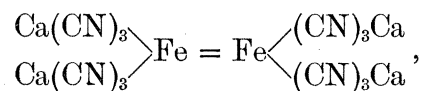
where $n (= 6)$ is the number of ions into which the molecule is split up; column (6) gives the observed osmotic equilibrium pressure.

TABLE IX.

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)
Weight concentration. Number of grammes of anhydrous salt to 100 gr. Aq.	Number of double gram-molecules in litre of solution. N.	Equivalent conductivity of the salt in solution. μ .	$\frac{\mu}{\mu_{\infty}}$.	Osmotic pressure calculated for 6 ions. P.	Observed osmotic equilibrium pressure. EP.
				atmospheres	atmospheres
Calcium Ferrocyanide.					
17·610	0·2926	0·01506	0·184	12·59	14·65
12·213	0·2055	0·01700	0·207	9·37	9·20
7·072	0·1203	0·01840	0·224	5·71	5·34
Strontium Ferrocyanide.					
23·99	0·3000	0·01452	0·167	12·33	12·04
17·97	0·2271	0·01603	0·184	9·77	8·59
13·01	0·1660	0·01702	0·196	7·37	6·18
6·180	0·0797	0·01816	0·209	3·65	3·40

If we take into consideration the various assumptions involved in calculating the numbers in column (5), the agreement between these and the observed osmotic pressures is as good as could be expected, but it should be mentioned that as good an agreement can be obtained if the double molecule be assumed to be split up into 5 ions.*

A simple chemical formula which will express these results is



where the ions are the four Ca and two $\text{Fe}(\text{CN})_6$, while a corresponding formula applies to the strontium salt. This formula was originally proposed by ERLÉNMEYER† for the ferrocyanides, and it is of interest to see whether, in the case of the potassium salt, a similar molecule, ionised into the corresponding number of ions, namely 10, will bring the calculated and observed osmotic pressures into agreement.

Using JONES and WEST's‡ measurements of the conductivities of potassium

* In this case the constitutional formula gives four Ca ions and one $\{\text{Fe}(\text{CN})_6\}_2$.

† 'Lehrbuch Org. Chem.,' 1867, p. 148.

‡ 'Amer. Chem. Jour.,' 34, 1809, p. 392.

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ferrocyanide solutions at 0° C. and treating the results in the same way as that adopted for the other salts, but keeping to their own units, we get for the double molecule and 10 ions the following table, where $\mu_{\infty} = 88.5$.

TABLE X.—Potassium Ferrocyanide.

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)
Weight concentration. Number of grammes of anhydrous salt to 100 gr. Aq.	Number of double gram-molecules in litre of solution. N.	Equivalent conductivity of the salt in solution. μ .	$\frac{\mu}{\mu_{\infty}}$.	Osmotic pressure calculated for 10 ions. P.	Observed osmotic equilibrium pressure. EP.
13.580	0.17735	40.1	0.453	atmospheres 20.18	atmospheres 19.25
8.897	0.1181	40.6	0.459	13.57	13.52
5.631	0.0756	41.7	0.471	8.88	9.19
3.035	0.04108	43.9	0.496	5.03	5.41
1.518	0.02064	47.7	0.539	2.72	2.93

The agreement between the numbers in columns (5) and (6) seems good enough to warrant the conclusion that the assumption of double* molecules ionised into 10 ions is not incompatible with the facts. On the other hand, it may be pointed out that the deviation from the theoretical BOYLE'S law osmotic pressure may be considerable, for it is apparent in cane-sugar solutions even down to some 7 atmospheres pressure; in view of the uncertainty of the value of the conductivities at infinite dilution, together with the weakness of the theory which connects them with the conductivities of the solutions themselves, it was considered useless to attempt to correct for these deviations.

Reviewing the evidence recorded in this communication, it may be concluded that the calcium and strontium salts are proved to be associated when in solution, and it is possible that they exist as the double molecules of the formula given on p. 335.

* Cp. BUCHBÖCK'S work on aqueous solutions of tetraethyl ferrocyanide ('Zeit. Phys. Chem.,' 23, 1897, p. 157), shows the molecule to be $(C_2H_5)_2Fe(CN)_6$. In view of the known tendency for organic isocyanides to be formed from certain metallic cyanides, it may be that this substance is constituted differently to the metallic ferrocyanides.